







Formation and agronomic efficiency of phosphorus-based fertilizer produced from cotton soapstock acidic wastewater and high-carbonate phosphorite

Sanjarbek Shamuratov^{1*} , Umidbek Baltaev¹ , Umarbek Alimov² ,
Akhrorjon Khoshimov³ , Azizbek Matmurov⁴ , Sherzod Kurambaev¹ 

¹ Urgench State University named after Abu Rayhon Biruni, Uzbekistan

² Institute of General and Inorganic Chemistry, Academy of Sciences of the Republic of Uzbekistan, Uzbekistan

³ The International Institute of Food Technology and Engineering, Uzbekistan

⁴ Mamun University, Khiva, Uzbekistan

* Corresponding author's email: shamuratovsx@gmail.com

ABSTRACT

In the conducted study, a phosphorus-based mineral fertilizer was obtained through the neutralization of acidic wastewater from cotton soapstock production using a mineral mass rich in carbonate from the Central Kyzylkum phosphorite deposit. The acidic wastewater was employed as a medium for the activation of partially inert phosphorite. The activation reaction was conducted at various mass compositions (from 100:10 to 100:40) and under controlled conditions (333 K, 300 rpm, and a reaction time of 30 minutes). The chemical composition of the products was investigated in terms of total phosphorus pentoxide (P_2O_5) content and bioavailable phosphorus in citric acid-soluble and Trilon B-soluble fractions. Optimal ratio conditions were achieved at a composition of 100:20, under which a desirable pH level and the highest bioavailable phosphorus content were obtained. The effect of the employed phosphorus fertilizer produced under optimal ratio conditions on agricultural growth was also demonstrated in tests involving cotton seeds. The tests clearly showed a significant increase in germination speed, length, and weight of the produced seeds in comparison to the control variant. The findings were further confirmed through statistical analysis ($p < 0.05$). This method is an exemplary and ecologically benign means of reutilization for industrial-scale acidic wastewater as well as phosphorite production waste in the synthesis of a highly valuable and useful phosphorus-based mineral fertilizer.

Keywords: acidic wastewater, phosphorite, P_2O_5 availability, mineral fertilizer, agronomic evaluation.

INTRODUCTION

Significance of phosphorus fertilizers and global resource scarcity

Phosphorus is considered one of the key biogenic elements, which is essential for plant energy metabolism as well as DNA synthesis (Cordell and White, 2014). Currently, agriculture is relying very largely on phosphorus-based fertilizers; however, its viability is often questioned, especially due to the impending depletion of phosphate rocks (Elser, 2012).

It was found that the viability of phosphate resources is at stake and that there are rapid changes

in the global production patterns of phosphates (Scholz and Wellmer 2013). It was also reported that there is inefficient use of phosphorus in all continents worldwide, and this overshoots because of excessive wastage (Withers, 2019). It was found that in the European Union, there are countries which import phosphorus that covers up to 90% of their demand (van Dijk et al., 2016). In these circumstances, recycling phosphorus from waste resources has emerged as one of the premier areas of scientific investigation worldwide (Zheng et al., 2022).

Global studies indicate that the large-scale application of phosphorus recycling technology

will play an important role in mitigating the problem of resource scarcity (Desmidt et al., 2015). In addition, it was mentioned that the future pattern of phosphate rock location will remain unstable and will create substantial economic risks in particular zones (Cooper et al., 2011). The warning signal about the exhaustion of natural phosphorus resources was first raised in “Nature”, and it was really an important warning signal concerning global food security (Gilbert, 2009). In the scientific community related to the subject of phosphorus, it was universally accepted that the problem of phosphorus resource management remains in its non-renewable character (Chowdhury et al., 2017). Therefore, phosphorus recovery in industrial wastewaters not only leads to the mitigation of the environmental problem, but also offers an opportunity to introduce the sustainable phosphorus source in agriculture (Zheng et al., 2022). In this respect, the recovery of phosphorus from wastewaters with high organic and inorganic components generated by technology will have an economic perspective (Desmidt et al., 2015).

There persists an ever-escalating need for phosphorus within the agricultural spheres across the globe to warrant the search for alternate phosphorus resources (Cordell and White, 2014). From the scientific evidence discussed above, the processing of wastewater containing acidic effluent from the fat and oil industry as well as phosphate rocks to make P_2O_5 fertilizer becomes an important scientific problem.

Acidic wastewater from the fat-and-oil industry and challenges of its treatment

The processing of fats and oils produces significant amounts of contaminated wastewater during various stages of vegetable oil processing as a consequence of chemical and thermal reactions. Amongst these effluents, the most troublesome waste is categorized as the acidic wastewater created during acid splitting of soapstock (He et al., 2025; Nourouzpour and Habibi, 2024; Javadzadeh et al., 2024)

The acidic wastewater generated in the acidulation of soapstock always tends to have pH range of 1–2 and thereby makes it an environmentally toxic liquid (Rifi et al., 2025) In addition, this acidic wastewater also possesses a significantly high amount of free fatty acids, phospholipids, proteins, gossypol residue, and emulsified oils. Additionally, because of its passage

from the neutralization units, it also tends to have a significantly high amount of cations like sodium, magnesium, and calcium in most cases beyond tolerated limits. Due to its high organic material and oil contents, there tends to be a significantly high chemical oxygen demand (COD) and biological oxygen demand (BOD), which exceeds standard limits. Upon release in water bodies, there tend to occur depletion of oxygen, putrefaction reactions, and changes in biological balance, thereby causing severe environmental problems (Louhichi et al., 2024; Saha et al., 2025; Chandrappa and Das, 2024).

In the existing situation, fat and oil processing plants use neutralization techniques to treat this kind of wastewater. Nevertheless, the method leads to the generation of high sludge volumes within the neutralization area. In addition, the strongly acidic pH enhances corrosion of various building materials, considerably shortening the technical lifespan of technical equipment. Furthermore, the high concentration of fatty acids and salts within the wastewater negatively impacts the efficiency as well as performance of various biological technologies (Khalidi-Idrissi et al., 2025; Shamuratov et al., 2025). In effect, the existing treatments of this kind of wastewater are economically inefficient. Nonetheless, the presence of a high volume of chemically active substances offers opportunities to view the wastewater as secondary raw materials (Sotimboev et al., 2024) The ability of the acidic medium to break down carbonate minerals makes it suitable and promising for use within the reaction medium of fertilizer processes due to the high potential of the method regarding technical and economic efficiency (Shamuratov et al., 2025; Sotimboev et al., 2024; Matchanov et al., 2025).

The processing capability of the mineralized mass of high-carbonate Central Kyzylkum

It should be noted that the phosphorites found in the Central Kyzylkum area have a high carbonate content, with calcium salts and apatite-like minerals being the chief constituents. It has been observed that if low-grade phosphorites are used directly as a fertilizer, the plant uptake of phosphorus can occur slowly, since these phosphorites have inefficient phosphate phases, which are less soluble. Nevertheless, if the low-grade phosphorites, named mineralized mass, are treated in the right manner, then their efficiency can be

heightened (Shamuratov et al., 2025; Otaboev et al., 2022; Seitnazarov et al., 2007).

The high content of carbonate in the mineral mass increases the reactivity of the mass in acidic solutions. This results in the breakdown of the mineral mass, hence increasing the probability of conversion of the phosphorus existing in insoluble states to a soluble state. The breakdown reaction of the carbonates in the acidic environment serves as a natural catalyst in the release of the phosphate ions. Also, other accessory minerals in the phosphorite transform in the presence of the acidic environment to give a new phosphate complex (Georgievskiy et al., 2024; Li et al., 2021; Wu et al., 2021).

Another benefit for low-grade phosphorites (mineralized mass) is their reactivity under acidic conditions without the need for substantial thermal processing and advanced technological treatment. This suggests that low-grade phosphorites are suitable for processing under the conditions of low energy consumption. The minerals in the mineralized mass are easily reactive with various industrial waste materials; therefore, there are high possibilities for creating multi-component phosphate complexes (Akhtamova et al., 2023). A significant amount of mineralized mass has been accumulated around the Central Kyzylkum phosphorite deposit as waste material. Taking into consideration that at present there are more than 13 million tons of such waste material in stockpiles, this material can be considered as inexpensive and scalable for processing (Tagayev et al., 2022).

On a whole, high-carbonate phosphorites possess a significant potential for conversion into efficient phosphorus fertilizers through processing together with some acidic technological streams. These fertilizers have been tested for agrochemical activity on various plants such as cotton, curcubit, and some common agricultural plants, and their applicability has been confirmed by results (Ergasheva et al., 2024; Turatbekova et al., 2024).

Interaction between acidic wastewater and phosphorite and formation of bioavailable P_2O_5 forms

In the acidic wastewater, the carbonates are rapidly dissolved from the phosphorite surface, thus chemically degrading the mineral lattice. This degradation of the mineral lattice due to the structural destabilization caused by the acidic

wastewater increases the mobility of the phosphate ions in the apatite-like salts. The ion exchange reactions due to the presence of acidic components in the cations of the acidic wastewater lead to the formation of more soluble phosphate compounds. In the reaction, the production of CO_2 further destabilizes the structural bonds in the mineral lattice. In the process, the presence of fluorescent ions results in the formation of new phases of fluorapatites, thus increasing the phase composition of the system. The depletion of the P_2O_5 level in the system also increases the share of the bioavailable soluble phosphorus content due to the processing of the acidic wastewater and the phosphorite (Shamuratov et al., 2025; Sotimboev et al., 2024)

Identification of research gaps

Although the general reaction characteristics for the interaction of phosphorite with various kinds of acid are known from the existing scientific literature, the reaction between high-carbonate phosphorite and the complex composition of the acidic wastewater from the fat-and-oil industry remains less explored (Shamuratov et al., 2025; Sotimboev et al., 2024). There are many publications on the phosphorite mineralogy, reactivity, and dissolution kinetics in sulfuric as well as nitric acids (Uktamov and Aliyeva, 2024; Gulzoda et al., 2025). However, there are not enough comprehensive studies on the phosphorite behavior in the multifaceted industrial waste media with both organic and inorganic components.

Moreover, although the current studies have proven the procedures to improve the solubility of phosphorus, they have not been able to explain the entire process of the transformation of P_2O_5 to the biological forms. In fact, most of the available studies conducted the reaction in the laboratory using pure chemicals, which means they had ignored the complex chemical reaction processes taking place when using real industrial wastewater. In particular, there are no conclusive results about the effect of organic acids, residual oils, cations, and auxiliary substances found in the acidic wastewater on the rate of decomposition of phosphorite.

Moreover, the agrichemical effectiveness of the phase generated in the reactivation of phosphorites has also not yet been adequately investigated. Thus, the above-mentioned scientific gap points to the urgency of a thorough study of the complex chemical interactions between

the acidic wastewater and high-carbonate phosphorite, the phosphate phase structure, the process of transformation of P_2O_5 into bio-effective forms, and the agronomic effectiveness of the generated material.

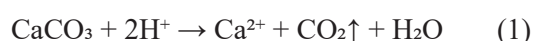
The research aim and scientific novelty

The main aim of this research was to establish the feasibility of obtaining bioavailable forms of P_2O_5 by assessing chemical interaction between the acidic wastewater of the fat and oil industries as well as high-carbonate phosphorite. The main aim was addressed by investigating the impact of wastewater acidity on phosphorite mineral composition, phosphate phase transformation conditions, as well as the agronomic utility of the prepared compounds. The scientific novelty of the presented research consists in the comprehensive study of the processes of conversion of phosphorus into biologically active compounds using the reaction of multicomponent acidic wastewaters with natural phosphorite. The obtained materials have undergone agrochemical analysis. The data have shown that due to the experimental treatment of the material with industrial wastewaters, the raw material has been upgraded into a compound containing phosphorus of great value in agriculture.

Reaction mechanism of phosphorite activation in acidic soapstock wastewater

Activation of high-carbonate phosphorite in acidic soapstock wastewater (AWW) is a process that occurs through an array of interconnected acid-base, dissolution-precipitation, ion exchange, and other reactions along the solid-liquid interface. Compared to the traditional activation that used one kind of mineral acid, the process in the context is more like a chemically complex bath containing inorganic acids, fatty acids, dissolved salts, as well as multivalent ions. These factors come into play in controlling the conversion of phosphorus to bioavailable forms.

Firstly, there is a rapid carbonate neutralization process within the mineralized mass (MM). The calcium and magnesium carbonates in this process easily interact with the acidic constituents present in wastewater, resulting in carbon dioxide gas as in this reaction:



The intense evolution of CO_2 gas causes micro-fracturing and weeping of the phosphorite matrix, thereby greatly increasing the reactive surface area of the apatite-like minerals. This mechanical weathering is an important factor that promotes the chemical changes by improving the accessibility of the phosphate groups entombed in the inert crystalline lattice.

Concomitant with these reactions is the proton penetration process that results in Ca-O-P bond weakening, causing phosphate ions to be attracted towards the liquid phase. It should be noted that when Ca-HAP is present under acidic conditions, lattice ion exchange results in a defluorination reaction, hence producing a less crystalline calcium phosphate. This is substantiated by the fact that when Ca-HAP is exposed to an acidic environment, its X-ray diffraction pattern becomes broad, indicating a decrease in crystallinity.

One of the characteristic features of the existing system is the participation of organic acids and amphiphilic substances of soapstock acidulation origin. Both free fatty acids and the remnant phospholipids function as proton donors as well as complexing agents for the Ca^{2+} and Mg^{2+} ions liberated by the decomposition of the carbonate materials. The presence of soluble or weakly bound complexes of mineral and organic substances lowers the likelihood of rapid re-precipitation of calcium phosphates, hence maintaining phosphorus in a more available form, which clearly distinguishes the acidic wastewater activation process from the traditional mineral acid treatment processes, whereby rapid re-crystallization generally restricts phosphorus availability.

A dynamic state of equilibrium between dissolution and re-precipitation reactions will be developed as the reaction progresses. With moderate values of pH near 5.5 to 6.0, corresponding to the optimum values for AWW:MM at 100:20, ill-crystalline calcium phosphate phases and amorphous phosphorus compounds are largely favored. These are the materials that display higher solubility properties to weaker extractants such as citric acid and EDTA (Trilon B), the acceptance of which as an indicator for agronomic phosphorus availability has generally been approved. Higher loads will give higher values for pH that are near neutral to slightly alkaline, thus inclining secondary re-precipitates towards the biologically less available fractions for P_2O_5 .

The activation process may be considered to comprise several steps, namely: (1) the fast

process of carbonate neutralization and structural breakdown due to the liberation of CO₂, (2) the breakdown process involving the liberation of cations from the apatite components due to the use of acid, (3) the process involving the complexation of the cations released from the breakdown process by the organic components in the wastewater, and (4) the final stabilization of phosphorus in weakly crystalline or amorphous form.

Pseudo-kinetic interpretation of the neutralization and phosphorite activation process

Neutralization reaction between the acidic soapstock wastewater and the high-carbonate phosphorite occurs in a time-dependent manner according to a heterogeneous process that follows the kinetics of the simultaneous breakdown of the carbonate and the lattice instability of the phosphate. Despite the complex reaction environment involving multi-components, the process of conversion pertaining to the availability of phosphorus can be explained in a pseudo-kinetic environment.

During the initial stage, it is observed that the rate of reaction is mainly controlled by the fast acid-carbonate reaction that takes place on the mineral surface. As a result of the high concentration of reactive carbonate, the rate of liberation of CO₂ becomes high, particularly for a chemically controlled regime. At this stage, it can be concluded that the diffusion of protons from the liquid phase to the solid phase becomes sufficiently fast.

As the reaction proceeds, the partial consumption of available carbonates and the buildup of products at the solid-liquid interface cause the system to transition towards the mixed kinetic control regime. At this point, the rates of surface kinetic processes and diffusion in the developed porous/amorphous interface control the rates of the main reaction. The generation of microporosity created by the release of CO₂ improves the rates of diffusion, hence hindering the full passivation of the phosphorite interface, leading to the continuous release of phosphate ions.

These reaction conditions obtained from the experiment (temperature: 333 K, time: 30 min) fit into this pseudo-kinetic model. Increasing the temperature also increases the proton mobility, thereby accelerating the dissolution of carbonate, thus decreasing the activation energy of the reaction at the interface. At the same time, the reaction

time should be long enough to establish a pseudo-equilibrium state, in which the greater fraction of the reactive form of carbonate has been converted, without over-producing the calcium phosphate in the secondary precipitation step. This is manifested in the peak yield of P₂O₅, as derived from the extraction using citric acid/EDTA at the optimal weight ratio of AWW:MM.

From a kinetic point of view, it can be modeled as a pseudo-first-order reaction with regard to the content of reactive carbonate, in which case the pseudo-first-order rate constant is composed of both reaction and diffusion terms. Although a proper kinetic analysis would need to be carried out using time-resolved experimental information, it is clear that phosphorus activation is optimized when both rates are similar.

At relatively high levels of mineral loading (AWW:MM > 100:30), a rapid rate of acidity consumption results in a pH increase, causing a movement towards a thermodynamically favored calcium phosphate re-precipitation process. Kinetically, there would be a reduction in the rate of formation of bioavailable phosphorus, as the new precipitates have higher crystallinity with lower solubility. Alternatively, when there is low mineral loading, there would still be a lack of activation.

In general, the pseudo-kinetic model verifies that the optimal conditions found do indeed reflect a balance between reaction rate and phase stability. The activation of phosphorite in the acidic soapstock wastewater is, in other words, dependent upon more than simple equilibrium, being a function of the dynamic changes in the reaction system itself, which determine the availability of P₂O₅.

MATERIALS AND METHODS

Materials used in the study

The whole study was based on two raw materials: the acidic wastewater (AWW), provided in the framework of soapstock acidulation line of “Urganich Yog’-Moy” JSC, and a high-carbonate mineralized mass (MM) – a product of the Central Kyzylkum phosphorite complex.

This acidic wastewater originated from the soapstock acidulation unit, which separates the fatty acids with concentrated sulfuric acid (H₂SO₄). The wastewater was directly fed from the processing stream to the lab without filtering,

and its properties were measured as follows: pH 2.0, with a strong color and smell, chemical oxygen demand (COD) of 947.2 mg O₂/L, biochemical oxygen demand over five days (BOD₅) of 380.2 mg O₂/L, total hardness between 56.50 and 108.50 mg-eq/L, and insoluble suspended solids at 6185 mg/L. It presented a complex cation-anion mix, mainly with Na⁺, Mg²⁺, Ca²⁺, and NH₄⁺ ions, besides SO₄²⁻, Cl⁻, and HCO₃⁻ anions. Organic matter represented 2.1% of the wastewater composition (Table 1).

The second raw material was a waste product obtained from the Central Kyzylkum phosphorite

complex, namely high-carbonate MM, which was extracted under natural conditions. For experimental purposes, the material was dried, sieved, and prepared prior to use. In terms of chemical composition, this mineralized mass contains CO₂, CaO, MgO, Fe₂O₃, Al₂O₃, and apatite-like phosphate phases (Table 1). The total P₂O₅ content was 15.09%, while the plant-available fraction accounted for 9.11%. The high carbonate content plays a significant role in the interaction with acidic wastewater, promoting CO₂ release and effective loosening of the phosphate lattice during the reaction process. Both materials were

Table 1. Integrated chemical and physical characteristics of AWW and M

Parameter group	Parameter	Unit	AWW value	MM value
General properties of AWW	pH	–	2.0	–
	Appearance	–	Reddish-brown	–
	Odor	–	Specific	–
	COD	mg O ₂ /L	947.2	–
	BOD ₅	mg O ₂ /L	380.2	–
	Total hardness (carbonate)	mg-eq/L	56.50	–
	Total hardness (non-carbonate)	mg-eq/L	108.50	–
	Total dissolved solids	mg/L	6185	–
	Suspended solids	mg/L	140.51	–
Cation composition of AWW	H ⁺	mg/L	100	–
	Na ⁺	mg/L	43,158	–
	Ca ²⁺	mg/L	300	–
	Mg ²⁺	mg/L	1,824	–
	NH ₄ ⁺	mg/L	100	–
	Fe ²⁺	mg/L	30	–
	Fe ³⁺	mg/L	0.3	–
Anion composition of AWW	Cl ⁻	mg/L	38,116	–
	SO ₄ ²⁻	mg/L	48,145	–
	NO ₃ ⁻	mg/L	840	–
	HCO ₃ ⁻	mg/L	3,446	–
Organic components in AWW	Organic matter	%	2.1	–
	Total SO ₃	%	1.64	–
Composition of mineralized mass (MM)	P ₂ O ₅ (available)	%	–	9.11
	P ₂ O ₅ (total)	%	–	15.09
	CaO	%	–	43.17
	MgO	%	–	1.21
	Fe ₂ O ₃	%	–	1.34
	Al ₂ O ₃	%	–	1.22
	CO ₂	%	–	14.01
	F ⁻	%	–	1.70
	SO ₃	%	–	2.17
	Moisture (H ₂ O)	%	–	1.02

used directly from their respective technological streams without additional purification.

It should be noted that the chemical composition of acidic wastewater from the oil and fat industry can vary depending on the seasonal quality of raw materials and technological conditions of operations. However, it is necessary to note that the phosphorite activation process presented in this study is mainly controlled by the total acidity of wastewater, rather than specific organic and inorganic compounds. The main process is based on the acid-carbonate neutralization reaction, which is effective over a wide range of wastewater compositions. To ensure repeatability of the process on an industrial scale, it is recommended that pH and total acidity of wastewater be monitored periodically.

This approach ensured the preservation of their intrinsic industrial characteristics and enabled a realistic assessment of the reaction behavior under conditions representative of actual industrial environments.

Experimental conditions and neutralization process

In this experiment, AWW and MM were added to a reactor vessel at various mass ratios of 100:10, 100:20, 100:30, and 100:40. They were mixed at 300 rpm for 30 minutes at 333K.

The selected reaction temperature (333 K) and reaction duration (30 minutes) were determined on the basis of specific kinetic considerations and preliminary observations. The reaction temperature was selected to allow for rapid reaction rates for the decomposition of carbonates and evolution of CO₂, thus ensuring effective disruption of the phosphorite matrix microstructure and increasing the accessibility of phosphate. The reaction was allowed to last for 30 minutes to enable completion of the primary reaction without allowing secondary recrystallization of calcium phosphates to occur. Longer reaction times or increased reaction temperature did not significantly improve the bioavailable P₂O₅ while increasing energy consumption.

In this study, 333 K was preferred, because it facilitates fast decomposition of carbonate, vigorous liberation of CO₂, as well as oxidation of apatite structures. At 300 rpm, complete interaction between the organic acids and mineral ions present in AWW, as well as those of phosphorite, was ensured. Additionally, 30 minutes was sufficient for complete decarbonization, partial

defluorination, as well as transformation of phosphate compounds into mobile phases. After this, filtration was performed, followed by drying at 353 K for further testing of analyses (Shamuratov et al., 2025; Sotimboev et al. 2024).

Chemical and X-ray phase analyses

The chemical composition of reaction products was also analyzed. The pH measurement was done by preparing an aqueous solution in a ratio of 1:10 in distilled water and then measuring potentiometrically (Rayimbekov, 2025).

For total P₂O₅, the dried samples were mineralized, and then spectrophotometry was carried out using the molybdenum phosphate complex. In order to assess the amount of available P₂O₅, the following extract procedures were adopted: (1) 2% citric acid-soluble P₂O₅, and (2) 0.2 M Trilon B (EDTA) extractable P₂O₅. In the procedures, the concentration of P₂O₅ was determined using spectrophotometry (Shamuratov et al. 2025; Sotimboev et al. 2024).

The CaO, SO₃, and MgO contents in the obtained product were determined by gravimetric and titrimetric analyses. To assess the decomposition of carbonates, the CO₂ content (decarbonization level) was measured using the traditional gas evolution technique [33].

The fluoride ion content was determined using an ion selective electrode. The organic material content of the products was determined using loss on ignition (LOI) at 550 °C. The chemical analysis was conducted in triplicates, and the average values are presented.

For phase composition, the technique of X-ray diffraction (XRD) analysis was employed to the phosphorus-rich products. Prior to carrying out the analysis, the dried samples were reduced to a fine powder and analyzed using the standard powder-diffraction technique. The results of the analysis revealed the major minerals, the extent of crystallinity, and new phases that may have resulted from the interaction of the acid and phosphorite.

The reduction in calcite peak intensity and the broadening of phosphate-related reflections indicate effective decarbonization and partial amorphization of the phosphorite matrix. Increased peak width reflects reduced crystallite size, which is directly associated with enhanced phosphorus bioavailability.

Methodology of agrochemical and biological tests

In order to assess the effect of the treated phosphorus fertilizers on the growth of plants, cotton seeds were used as the standard biological indicator. The phosphorus fertilizer solutions were made at a concentration of 0.002% and consisted of 2.8 grams per 100 mL of solution, while another at a concentration of 0.0002% and consisted of 280 mg. Prior to the testing, the seeds were washed using distilled water and placed on the filter paper to ensure uniform moisture content. The test was conducted using Petri dishes and carried out three times for each scenario. The Petri dishes were placed within the thermostat at 25 °C, and the germination was monitored for six days. Finally, the growth measurements were taken, including the average seed length and the fresh weight.

Statistical analysis

All the experiments were carried out under triplicate settings, and statistical means were used to determine reliability. For each parameter measured, both the average values and the standard deviation were calculated. In order to determine whether the results were statistically significant or not, analysis of variance, known as ANOVA, was conducted. The roles of both concentration and weight ratios were considered.

RESULTS AND DISCUSSION

Results of neutralization and selection of optimum mass ratio

AWW and the high-carbonate MM were tested for reactivity across a spanned range of mass ratios from 100:10 to 100:40. Following the reaction, we investigated various indicators: pH, organic matter, total and plant-available P_2O_5 , and the levels of CaO, SO_3 , CO_2 , and fluoride, as listed in Table 2.

The changes in the reaction medium followed the chosen mass ratio quite well. As the share of MM grew, the pH climbed from 4.10 to 7.30. The main neutralization came from the carbonates in MM reacting with the acids, and the released CO_2 affected the rearrangement of the apatite-like phases. The rearrangement favored the formation of plant available P_2O_5 forms. However, at low

MM input (100:10–100:15), too much acidity still remained, and the bioavailable P_2O_5 remained low. Higher MM loadings (100:30–100:40) drove the pH too high, with the result of re-precipitation of phosphate and consequently diminishing the plant-available phosphorus fractions.

The best performance appeared at a 100:20 mass ratio. This mix achieved the most favorable balance: it supported higher total P_2O_5 , promoted the citric acid-soluble fraction, favored EDTA-soluble (Trilon B-extractable) phosphorus, and maintained a stable overall pH, marking it as the optimal processing condition.

Results of X-ray diffraction (XRD) analysis

The dried sample, with an optimal ratio of AWW:MM of 100:20, was assessed for changes in its mineral composition through XRD with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$), voltage of 40 kV, and a current of 30 mA scanning from $2\theta = 5^\circ$ to 70° (as shown in Figure 1).

The diffractogram reveals the presence of a number of strong peaks which occur alongside a decrease in the number of reflections associated with some initial phases, which indicates a high degree of rearrangement in the mineral environment to achieve a neutral environment. It should be noted that strong peaks around 2θ values of $29\text{--}32^\circ$ confirm the development of apatite-like phases and calcium phosphate phases. The peaks with varying FWHM values confirm a lattice with some irregularities and the development of new phases with smaller crystallites.

With the help of the peaks in Figure 1 above, the major peaks relate to interplanar distances of $d \approx 3.04 \text{ \AA}$, 2.80 \AA , as well as 3.08 \AA . These are common in phosphate minerals (Table 3).

This indicates that there was partial activation of the phosphate minerals that were inert in the high-carbonate phosphorite in the acidic media. Conversely, the decrease in the carbonate-related peaks indicates decarbonization.

To conclude, the analysis of the XRD patterns reveals that the process of neutralization conducted at a mass ratio of 100:20 causes a notable change to the mineral composition of phosphorite, which means that the carbonate minerals are decomposed and the phosphate materials are recrystallized into a new reactive form (Figure 2).

The reduced background scattering and increased widths of the diffraction peaks indicate the presence of higher concentrations of

Table 2. Chemical characteristics of the products obtained from the neutralization process

AWW:MM	pH	Organic substance, %	P ₂ O ₅ total, %	P ₂ O ₅ (citric acid), %	P ₂ O ₅ (Trilon-B), %	CaO, %	SO ₃ , %	CO ₂ , %	F, %
100:10	4.10	11.39	8.19	3.81	2.41	23.92	10.81	4.41	1.07
100:15	4.81	8.82	9.51	3.47	2.40	27.95	8.92	9.30	1.16
100:20 (optimal)	5.62	7.23	10.42	3.02	2.21	28.66	6.96	6.16	1.27
100:25	5.90	6.22	11.16	2.61	2.17	32.68	6.42	7.99	1.42
100:30	6.33	5.41	11.67	2.21	2.08	35.48	5.45	7.81	1.39
100:35	6.74	6.21	12.18	2.15	2.02	36.74	5.16	8.54	1.38
100:40	7.30	4.34	12.49	2.02	1.98	36.96	4.68	9.15	1.40

amorphous substances, which are desirable for the formation of P₂O₅ molecules more readily available to plants. Such a result proves that the mass ratio is optimal and that phosphorus fertilizer materials are produced.

Results of agrochemical tests

The agronomic utility of the produced phosphorus mineral fertilizer was determined using seed germination, potential for germination, and seedling growth. Control experiments involved soaking the seeds in distilled water, whereas the experimental setups involved using varying fertilizer concentrations (as shown in Tables 4 and 5 and Figure 3). The experiments were performed in a triplicate setting, and data was presented using means, SD, and ANOVA.

Table 4 reveals that a fertilizer dose of 0.0002% maintained the germination parameters. A diminished dose of 0.00002% slightly decreased the germination ability. One-way ANOVA analysis demonstrated significant variations in different concentrations ($p < 0.05$), which presented a noticeable and scientifically linked effect related to the dose level.

It is clear from Table 5 that the increase in the average seedling length and biomass for concentration 0.0002% was 1.7 times the control and positive, respectively. The low SD values indicate good reproducibility, and ANOVA indicated the significance of differences between the treatments and the control for seedling length and plant biomass ($p < 0.05$).

In sum, the agrochemical test results show that the phosphorus mineral fertilizer activated via the action of acidic wastewater with a mass ratio of 100:20 possesses high biological properties. Thus, at a concentration of 0.0002%, it showed a significant positive effect during seedling growth.

In light of these findings, it can be upheld that the available phosphorus compounds in P₂O₅ of the fertilizer are efficiently taken up by seedlings and that its agronomic applicability is valid.

Expanded and critical discussion

These findings confirm that the levels of phosphorite activation achievable in the acidic soapstock wastewater remain remarkably sensitive to the interaction of chemical treatments, the transformation processes, and secondary precipitation. Although the tested AWW:MM ratios of wastewater successfully accelerated the transformation of the inert phosphorus species to bioavailable species, the specific ratio of 100:20 played an important role at the boundary of these antagonistic factors.

For lower loadings of minerals (AWW-MM = 100:10-100:15), the prevailing acidic condition continues until the end of the reaction. Even as the process of the dissolution of carbonates has been initiated, the unavailability of reactive minerals counters the degree of destabilization in the lattice structure of apatite. Consequently, the liberation of phosphates has not been complete, and phosphorus has been present in more stable forms as minerals. This justifies the lower values for citric-acid- and EDTA-soluble P₂O₅.

On the other hand, an excessive augmentation of the mineralized component above the optimal proportion (AWW:MM > 100:30) causes a swift uptake of acidity along with a corresponding increase in pH. Indeed, a suitable reaction environment emerges in this case, being preferable for the re-precipitation of calcium phosphate phases of increased crystallinity. The latter phases are, in turn, more stable in a thermodynamical sense, but less soluble in weak extractants, which directly corresponds to a noted decrease in the plant-available

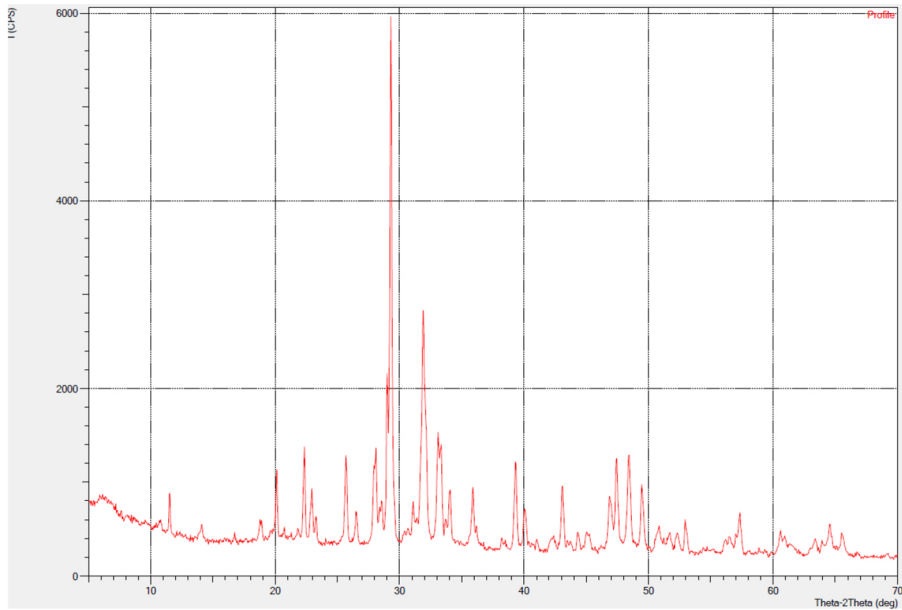


Figure 1. X-ray diffraction (XRD) pattern of the product obtained by neutralization of acidic wastewater with the Central Kyzylkum phosphorite at a mass ratio of 100:20 (dried sample)

Table 3. Main diffraction peaks and phase assignment of the dried product (AWW:MM = 100:20)

No.	2θ (deg)	d-spacing (Å)	Relative intensity (%)	Assigned phase
1	29.32	3.04	100	Calcite (CaCO ₃)
2	31.93	2.80	44	Fluorapatite (Ca ₅ (PO ₄) ₃ F)
3	28.99	3.08	30	Apatite-type phosphate
4	25.73	3.46	16	Calcium phosphate
5	39.32	2.29	19	Calcite (CaCO ₃)

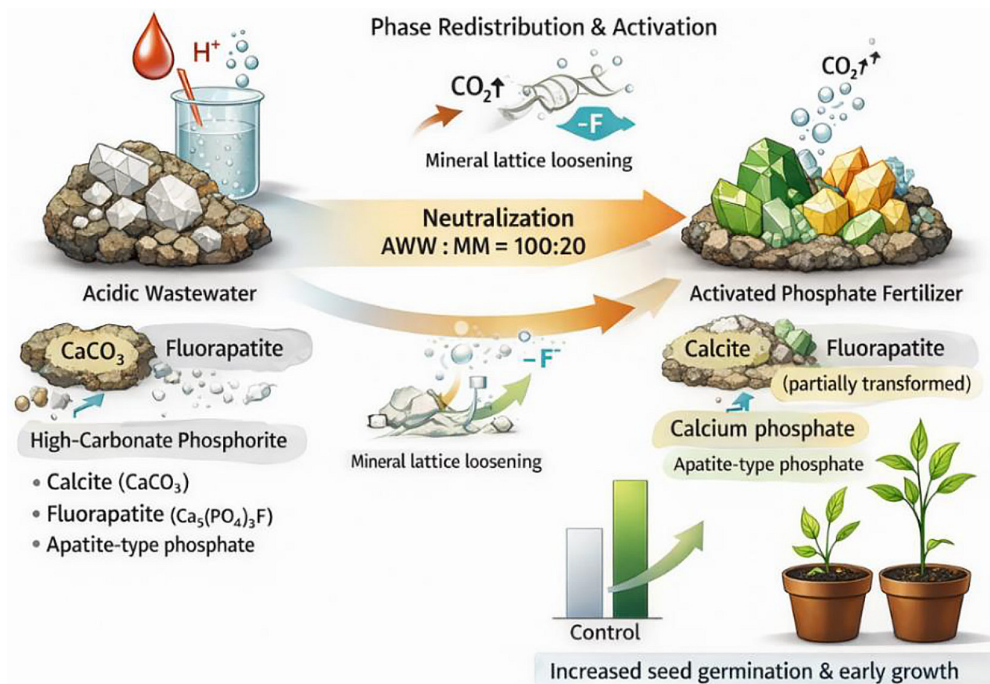


Figure 2. Phase transformation of high-carbonate phosphorite during acidic wastewater neutralization (AWW:MM = 100:20)

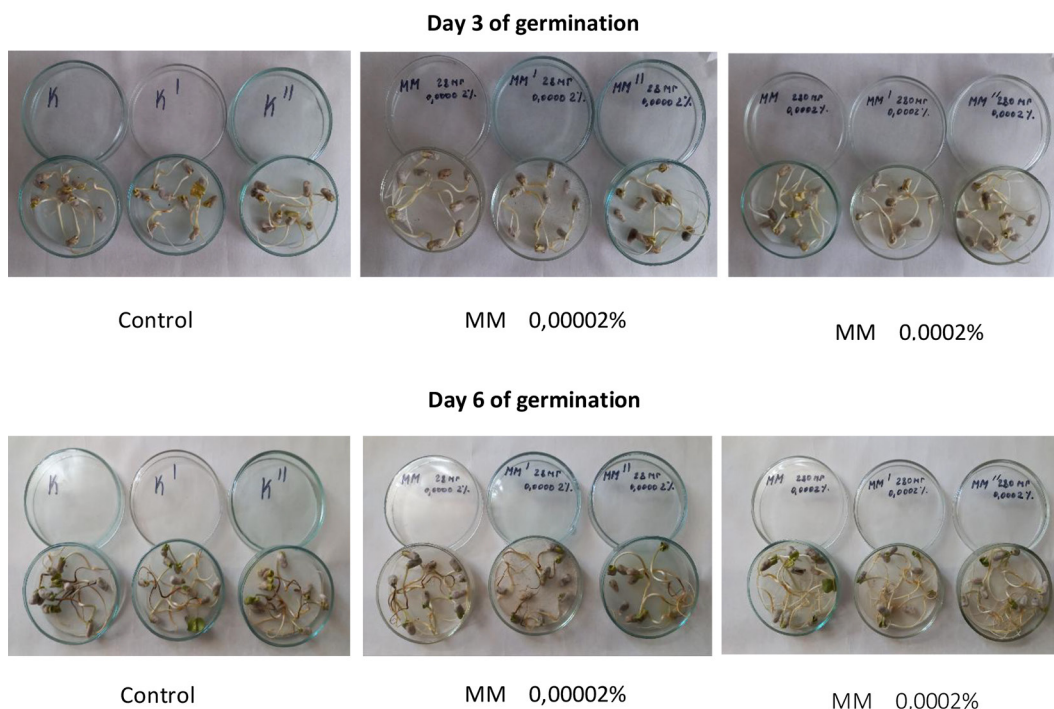


Figure 3. Germination of cotton seeds on the 3rd and 6th day under different fertilizer concentrations

phosphorus forms. This can be seen as a two-sided function of calcium ions, on the one hand participating in the formation of phosphate phases, but on the other hand, their accumulation favors phase stability but not activation.

The advantage in the 100:20 mass ratio can thus be ascribed to its capacity to create the optimal pH conditions where the processes of the decomposition of carbonates, the destabilization of apatite, and the inhibition of secondary crystallization can proceed concurrently. The data obtained in the XRD experiment tend to bear out this explanation in view of the fact that the diffraction intensity

of the calcite peaks became reduced and the peaks associated with phosphates became broader, which can be attributed to the reduced crystallinity or the amorphicity observed in the samples.

The structural characteristics mentioned above are generally known to offer favorable conditions for the bioavailability of phosphorus in the soil because the phases or structures in the sample, being more amorphous or less crystalline in nature, become more easily liable to the action of the organic chelating agents normally present.

An important factor that sets the new system apart from the typical mineral acid process

Table 4. Effect of mineralized mass (MM) on cotton seed germination and emergence

Experimental variant	Fertilizer concentration	Germination rate, % (3rd day)	Emergence rate, % (6th day)	Mean ± SD
Control (water)	–	93.33	93.33	93.33 ± 0.00
MM	0.0002% (280 mg)	83.33	90.00	86.67 ± 3.82
MM	0.00002% (28 mg)	70.00	80.00	75.00 ± 5.00

Table 5. Effect of mineralized mass (MM) on seedling length and biomass of cotton

Experimental variant	Fertilizer concentration	Mean seedling length, cm	Mean biomass, g	Mean ± SD
Control	–	8.53	0.194	8.53 ± 0.19
MM	0.0002% (280 mg)	14.88	0.227	14.88 ± 1.23
MM	0.00002% (28 mg)	8.86	0.173	8.86 ± 1.54

is the complex nature of the composition of the acidic water. Organic acids and amphiphilic compounds, which result from the soapstock acidulation process, seem to have a stabilizing effect on Ca^{2+} and Mg^{2+} ion release. The effect is that the phosphorus compounds remain in a mobile form and that the process takes advantage of a synergistic effect, which is not possible in solitary acid processes.

The agronomic results also verify the physicochemical data. The increased germination speed, seedling height, and biomass at low fertilizer concentrations demonstrate that the activated phosphorus becomes readily available at the beginning phases of plant growth. This satisfies the principles for phosphorus nutrition, wherein availability at the beginning phases is considered more essential than phosphorus concentration. The fact that the differences are significantly distinct between the treated groups and the control ensures that the activation attained is characterized by the properties that go beyond chemical properties and are indeed agronomic.

However, despite the encouraging outcomes, some limitations in the current study must be pointed out. The laboratory analyses were carried out under controlled conditions, and even though the study employs the use of wastewater from an industry, some scale-related characteristics, such as the intensity of mixing and the differences in the wastewater constitution, could affect the process in an industrial setting. There is also a lack of studies regarding long-term soil interactions and phosphorus fixation.

Practically, the proposed process provides a viable route to the valorization of two challenging wastewaters: the acidic wastes of the fat/oil industry, as well as low-grade carbonate-rich phosphorite wastes. As the process combines the concept of neutralization of wastes with the production of fertilizers, it acts as an efficient process in the mitigation of the problem of wastes as well as the efficient use of resources. The process has the advantage of being carried out in simpler process conditions, with no mineral acid being involved.

The broader analysis above serves to affirm the fact that the processing of high-carbonate phosphorite in soapstock wastewater media requires a complex interplay among the kinetics and stability conditions. The search for the optimal processing conditions reveals the significance of control both in the chemistry and in the kinetics involved in the search for sustainable

fertilizers for phosphorus. Though a direct comparison with commercial superphosphate-based fertilizers was not the objective of this study, the determined citric acid- and EDTA-soluble P_2O_5 contents are comparable with those of partially acidulated phosphate-based fertilizers. The observed positive effects of the developed fertilizer on seed germination and seedling growth confirm the agronomic efficacy of the fertilizer. Comparative field-scale tests with commercial phosphate-based fertilizers are planned for future work.

The method of phosphorite activation can be applied to other acidic wastewaters from industrial sources if there is sufficient acidity to start the dissolution of carbonate and apatite. Metallurgical wastewaters may need further treatment because of the presence of heavy metals or toxic ions. On the other hand, the wastewaters from the food industry and fat and oil industry are more suitable because of lower toxicity and the presence of organic acids that help in ion complexation.

CONCLUSIONS

This research has shown that the acidic wastewater formed in the process of cotton soapstock treatment by acid can be effectively used as the reactive medium for activating the high-carbonate phosphorite mass in the Central Kyzylkum Region phosphorites. With the influence of the acidity environment, the carbonate fractions undergo decomposition and the release of CO_2 gas that helps in the transformation of the inert P_2O_5 into the plant-accessible fractions.

Of all the investigated mass ratios of acidic wastewater to mineral mass (AWW:MM), a ratio of 100:20 was determined as optimal, achieving a balance with respect to total P_2O_5 and fractions soluble in citric acid and EDTA (Trilon B). X-ray diffraction analysis revealed a creation of new phosphates and a strong modification of the initial carbonate-rich matrix of the activated material.

Agrochemical tests revealed the potential of the phosphorus mineral fertilizer derived from the phosphorite waste in optimizing the germination of seeds, the rate of germination, as well as the growth of the germinated seeds. In a general sense, the results are a scientific basis for the effective use of phosphorite waste as a precious asset and a catalyst in the development of environmentally sustainable phosphorus fertilizers.

REFERENCES

1. Akhtamova, M., Temirov, U., Khurramov, N., Shukurov, A., Karshiev, B. (2023). Processing of phosphorites and additives with researching their thermodynamical properties. (O. Tursunov, Ed.), *E3S Web of Conferences*. EDP Sciences. <https://doi.org/10.1051/e3sconf/202343403016>
2. Chandrappa, R., Das, D.B. (2024). *Waste from Industry and Commercial Activity*. In: Solid Waste Management. Environmental Science and Engineering. Springer, Cham. https://doi.org/10.1007/978-3-031-50442-6_9
3. Chowdhury, R. B., Moore, G. A., Weatherley, A. J., Arora, M. (2017, January). Key sustainability challenges for the global phosphorus resource, their implications for global food security, and options for mitigation. *Journal of Cleaner Production*. Elsevier BV. <https://doi.org/10.1016/j.jclepro.2016.07.012>
4. Cooper, J., Lombardi, R., Boardman, D., Carliell-Marquet, C. (2011). The future distribution and production of global phosphate rock reserves. *Resources, Conservation and Recycling*, 57, 78–86. <https://doi.org/10.1016/j.resconrec.2011.09.009>
5. Cordell, D., White, S. (2014). Life's bottleneck: Sustaining the world's phosphorus for a food secure future. *Annual Review of Environment and Resources*, 39, 161–188. <https://doi.org/10.1146/annurev-environ-010213-113300>
6. Desmidt, E., Ghyselbrecht, K., Zhang, Y., Pinoy, L., Van der Bruggen, B., Verstraete, W., Rabaey, K. (2015). Global phosphorus scarcity and full-scale P-recovery techniques: A review. *Critical Reviews in Environmental Science and Technology*, 45(4), 336–384. <https://doi.org/10.1080/10643389.2013.866531>
7. Elser, J. (2012). Phosphorus: A limiting nutrient for humanity? *Current Opinion in Biotechnology*, 23(6), 833–838. <https://doi.org/10.1016/j.copbio.2012.03.001>
8. Ergasheva, O., Qarshiboyev, S., Husanova, S., Atashev, E., Toshpulatov, N., Yuldosheva, C., & Mustofoyev, G. (2024). Study on the influence of fertilizers on the yield and quality of barley and potatoes. (O. Tursunov, Ed.), *E3S Web of Conferences*. EDP Sciences. <https://doi.org/10.1051/e3sconf/202449703013>
9. Georgievskiy, A.F., Bugina, V.M., Georgievskiy, A.A. et al. (2024). New industrial genetic type of the ediacaran aphanitic phosphorite deposits. *Lithol Miner Resour* 59, 462–478 <https://doi.org/10.1134/S0024490224700561>
10. Gilbert, N. (2009). Environment: The disappearing nutrient. *Nature* 461, 716–718. <https://doi.org/10.1038/461716a>
11. Omonnayeveva, G., Usmanov, B., Khamrakulova, M., Sattarova, B., Kadirova, N. Chemical innovations in fertilizer production using Central Kyzylkum phosphorites. *AIP Conf. Proc.* 21 July 2025; 3304 (1), 040016. <https://doi.org/10.1063/5.0270938>
12. He, Z., Chen, T., Jin, W. et al. (2025). Optimization of degumming and deacidification processes for coffee oil. *Food Biophysics* 20, 139 <https://doi.org/10.1007/s11483-025-10023-6>
13. Javadzadeh, S., Almasi, H., Alizadeh-Khaledabad, M. et al. Immobilization of Al₂O₃ and Fe₃O₄ nanoparticles on cellulose and chitosan nanopapers for selective adsorption of free fatty acids from edible oil. *Polym. Bull.* 81, 2043–2067 (2024). <https://doi.org/10.1007/s00289-023-04798-2>
14. Khalidi-Idrissi, A., Hartal, O., Madinzi, A. et al. Natural flotation and coagulation–flocculation: a dual approach to refinery wastewater treatment. *Euro-Mediterr J Environ Integr* 10, 1425–1443 (2025). <https://doi.org/10.1007/s41207-024-00558-4>
15. Li, X., Huang, R., Wu, Q. et al. (2021). Experimental approach for the characterization of low-grade phosphate ore performance in isothermal conditions. *J. Sustain. Metall.* 7, 1736–1747. <https://doi.org/10.1007/s40831-021-00451-2>
16. Louhichi, G., El Khouni, A., Ghrabi, A. et al. (2024). Phytotoxicity assessment of treated vegetable oily wastewater via environmentally coagulation/flocculation and membrane filtration technologies using lettuce (*Lactuca sativa*) seeds. *Environ Sci Pollut Res* 31, 57204–57228. <https://doi.org/10.1007/s11356-023-31594-2>
17. Matchanov, S., Ruzmetova, A., Yakubov, Y. (2025). Experiments on bleaching of kaolin from the Khodjakulskoye deposit. (M. T. Chaichan, A. Rajabifard, T. Nirmalathas, M. M. Ahmad, S. Hong, & L. A. Kaushal, Eds.), *E3S Web of Conferences*. EDP Sciences. <https://doi.org/10.1051/e3sconf/202563306003>
18. Nourouzpour, M.M., Habibi, A. (2024). Degumming process of vegetable oil soap stocks and their applications to biological surfactant production by *Candida catenulata*. *Waste Biomass Valor* 15, 1339–1353. <https://doi.org/10.1007/s12649-023-02222-4>
19. Otabojev, K.A., Sherkuziev, D.S., Badalova, O.A. et al. (2022). Mineralogical composition of kyzylkum washed dry concentrate and its processing into simple superphosphate. *Russ J Gen Chem* 92, 505–517. <https://doi.org/10.1134/S1070363222030203>
20. Raiymbekov, Y. (2025). *Literature Review*. In: Enrichment of Low-Grade Phosphorites with Organic Acids. Springer, Cham. https://doi.org/10.1007/978-3-032-02910-2_2
21. Rifi, S.K. et al. (2025). *Study of the Performance of the Wastewater Treatment Plant in the Vegetable Oil Refining Industry*. In: Souabi, S., Anouzla, A.,

- Yadav, S., Singh, V.P., Yadava, R.N. (eds) Wastewater Treatment Plants. Water Science and Technology Library, 130. Springer, Cham. https://doi.org/10.1007/978-3-031-87461-1_3
22. Saha, B., Saha, R., Patra, D., Mohapatra, R.K. (2025). *Conversion of Oils and Fat Waste to Chemicals and Biofuels*. In: Kumari, A., Rai, M.P., Veeramuthu, A., Mishra, A. (eds) *Valorization of Solid Wastes to Biofuels and Chemical Products for Sustainable World*. Springer, Singapore. https://doi.org/10.1007/978-981-96-8594-3_8
 23. Scholz, R. W., Wellmer, F.-W. (2013, February). Approaching a dynamic view on the availability of mineral resources: What we may learn from the case of phosphorus? *Global Environmental Change*. Elsevier BV. <https://doi.org/10.1016/j.gloenvcha.2012.10.013>
 24. Seitnazarov, A.R., Musaeva, S.A., Namazov, S.S. et al. (2007). Mechanochemical activation of ordinary phosphorite powder of Central Kyzylykum mixed with urea nitrate and ammonium carbonate salts. *Russ J Appl Chem* 80, 1973–1976. <https://doi.org/10.1134/S1070427207110432>
 25. Shamuratov, S., Alimov, U., Rifky, M., Baltaev, U., Ibragimova M., Kurambaev, S., Radjabov M. (2025). Investigation of the kinetics of cotton soapstock saponification under ultrasonic illumination. *Eurasian Chemico-Technological Journal*, 27(4), 323–335. <https://doi.org/10.18321/ectj1679>
 26. Sotimboev, I., Baltaev, U., Shamuratov, S., Shamsiddin, R., Alimov, U., Saporboyev, M. (2024). Technical and economic efficiency of processing acidic wastewater from the oil and fat industry into necessary agricultural products. (O. Tursunov & Y. Zhou, Eds.), *E3S Web of Conferences*. EDP Sciences. <https://doi.org/10.1051/e3sconf/202456303072>
 27. Tagayev, I., Doniyarov, N., Asrorov, A., & Murodov, I. (2022, April 5). The role of medium condition for uranium separation from Central Kyzylykum's low-grade phosphorite after sulfuric acid treatment. *International Journal on Advanced Science, Engineering and Information Technology*. Insight Society. <https://doi.org/10.18517/ijaseit.12.2.14060>
 28. Turatbekova, A., Abdukadirova, M., Shamuratov, S., Latipov, B., Saporboyev, M., Shamshiyev, J., Makhmudov, Y. (2024). Investigation of the effect of fertilizers on the biochemical and physical characteristics of carrots (*Daucus carota* L.). (O. Tursunov & Y. Zhou, Eds.), *E3S Web of Conferences*. EDP Sciences. <https://doi.org/10.1051/e3sconf/202456303074>
 29. Uktamov, D., Aliyeva, M. (2024). Technology of obtaining micronutrient fertilizers based on micronutrient secondary raw materials of the industry. (I. Kovalev, Ed.), *E3S Web of Conferences*. EDP Sciences. <https://doi.org/10.1051/e3sconf/202448605023>
 30. van Dijk, K. C., Lesschen, J. P., Oenema, O. (2016). Phosphorus flows of European Union Member States. *Science of The Total Environment*, 542, 1078–1093. <https://doi.org/10.1016/j.scitotenv.2015.08.048>
 31. Withers, P.J.A. (2019). Closing the phosphorus cycle. *Nat Sustain* 2, 1001–1002. <https://doi.org/10.1038/s41893-019-0428-6>
 32. Wu, Q., Li, J., Lv, X. et al. (2021). Reaction Mechanism of Low-Grade Phosphate Ore During Vacuum Carbothermal Reduction. *Metall Mater Trans B*, 52, 1484–1494. <https://doi.org/10.1007/s11663-021-02117-6>
 33. Zheng, Y., Wan, Y., Zhang, Y., Huang, J., Yang, Y., Tsang, D. C. W., Wang, H., Chen, H., Gao, B. (2022). Recovery of phosphorus from wastewater: A review based on current phosphorous removal technologies. *Critical reviews in environmental science and technology*, 53(11), 1148–1172. <https://doi.org/10.1080/10643389.2022.2128194>